

PATENT SPECIFICATION

783,868



Data of Application and filing Complete Specification Oct. 5, 1955.

No. 28,89/55.

Application made in United States of America on Oct. 6, 1951.

Complete Specification Published Oct. 2, 1957.

Index at Acceptance:—Classes 1(2), A13; and 2(7), T8(D11: F1: F2: G3: K2B: K5: K8B).

International Classification:—C01b. C08g.

COMPLETE SPECIFICATION

A Process of preparing Hydrophobic Organo-Silicon Powders

We, MIDLAND SILICONES LIMITED, a British Company, of 19, Upper Brook Street, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel process for preparing hydrophobic organosilicon powders.

Finely divided silica has long been known and is widely used in industry. Such silica has been found as a natural resource and is known as diatomaceous earth, but the demand for a steady supply of pure silica powder has led to the development of method for preparing such materials synthetically. For example, certain volatile silicon compounds can be burned to produce fume silicas. Another method for preparing the desired silicas involves the drying of silica hydrogels (i.e. a gel composed of silica and water). However, when such hydrogels are air dried, the resulting product is a relatively coarse material having a bulk density in the range of from 0.7 to 1 gram per cc. Thus special techniques for drying the silica hydrogel have been evolved and the resulting silicas are known as aerogels and have a bulk density of about 0.09 gram per cc. The special techniques for preparing silica aerogels are uneconomic because of the necessity for using special pressure equipment and the relative complexity of the method as well as large loss of expensive solvent and diluent. The development of another technique in which pressure equipment was not required resulted in preparing a silica powder now known as a xerogel and having a bulk density in the range of 0.09 to 0.70 gram per cc.

We have been particularly interested in producing silica powders for use as fillers in siloxane elastomers. Certain silicas (i.e. those having a heat of wetting by water of from 0.3 to 1.0 calorie per cc. of pore volume) have long been known to be reinforcing fillers for such elastomers, and their use resulted in superior physical properties in the ultimate vulcanised silicone rubber. These reinforcing silicas are fully described in our Specification No. 582,540.

It has now been found that the xerogels are not, of themselves, reinforcing fillers for siloxane elastomers. However, xerogels modified in accordance with the process of our Specification No. 682,574 have been shown to have the desired reinforcing characteristics. The process for preparing such modified silica xerogels as heretofore disclosed involved reacting certain defined alkoxy silanes or chlorosilanes with a silica organogel. This process is commercially unattractive because of the expense in both time and money as well as the complexity of the process.

It is an object of this invention to prepare silica fillers which will produce a reinforcing action when incorporated in siloxane elastomers. Another object is to provide silica fillers which are equal or superior for use in siloxane elastomers to those heretofore employed. Another object is to produce treated xerogel silicas at a commercially feasible cost and by a relatively simple process.

In accordance with this invention, hydrophobic organo-silicon powders as prepared by reacting, (1) an organosilicon compound of the general formula $R_nSiO_{n/2}$ in which each

2

R is an aliphatic hydrocarbon radical containing less than 5 carbon atoms or a phenyl radical, there being not more than 1 phenyl attached to each silicon atom, and n has an average value of from 2 to 3 inclusive, with (2) an organogel in which at least 50 mol per cent of the polymer units are SiO_2 units, any remaining polymer units being of the general formula $R'SiO_{n/2}$ in which R' is an aliphatic hydrocarbon radical containing less than 5 carbon atoms, said organogel (2) having a density of from 0.02 to 0.35 g. per cc., and said organosilicon compound (1) being present in an amount such that there is at least 0.04 organosilyl units of compound (1) per polymer unit of the organogel (2). The reaction is catalysed with a strong acid. After the reaction is complete, the volatile materials are removed from the organogel and a dry powdery material having a bulk density of less than 0.59 per cc. is obtained.

It is known in the art that organogels can be prepared from hydrogels by replacing the water in the hydrogel with an organic solvent. During this replacement there is little or no shrinkage of the gel so that the density of the organogel is the same as that of the original hydrogel. The organogels (2) which are employed in this invention can be either silica organogels or co-gels of silica and monoorganosiloxanes. The silica organogels are best prepared from sodium silicate by acidifying a solution of the latter, allowing the silica to gel and thereafter replacing the water in the gel interstices with an organic solvent. The co-gels are best prepared by acidifying a solution of a mixture of sodium silicate and a salt of the general formula $R'Si(ONa)_xO_{1-x}$ in which

2

x has a value from 1 to 2. Upon acidification of such a solution, a co-gel will be obtained in which some of the gel units are SiO_2 and the remaining units are $R'SiO_{1.5}$. Thus the co-gels are actually co-polymers of silica and monoorganosiloxanes. The water in the interstices of the co-gel is then replaced by an organic solvent.

In all cases the organogels employed in this invention should have densities of from 0.02 to 0.35 gram per cc. The density of the gel has reference to the grams of total SiO_2 plus $R'SiO_{1.5}$ per cc. of gel.

For the purpose of this invention monoorganosiloxanes which may be co-polymerised with the SiO_2 in organogel (2) are those having aliphatic hydrocarbon radicals containing less than 5 carbon atoms attached to the silicon. Specific examples of such materials are monomethylsiloxane, monopropylsiloxane, monovinylsiloxane, monoallylsiloxane and monobutyl siloxane and combinations thereof.

For the purpose of this invention compound (1) must be present in amount sufficient that there is at least 0.04 organosilyl groups (i.e. $R'Si=$ or $R'Si-$) per polymer unit in (2) (i.e. based on total SiO_2 plus $R'SiO_{1.5}$ in 2). If compound (1) is present in amount less than the specified amount, the resulting material does not have the reinforcing action desired for siloxane elastomers. However, any amount of organosilicon compound (1) above that above-defined amount may be employed without deleteriously affecting the reinforcing action of the silica. In those cases where an excessive amount of organosilicon compound (1) is employed, say 15 to 20 organosilyl units per polymer unit in (2), it merely acts as a solvent.

It has been found that any organosiloxane can be made to react with silica gels or co-gels. However, for the purpose of this invention the R groups in organosilicon compound (1) must be aliphatic hydrocarbon radicals containing less than 5 carbon atoms or phenyl radicals. However, there should be not more

than 1 phenyl radical attached to each silicon. In all cases there should be from 2 to 3 inclusive of the defined hydrocarbon radicals per silicon atom.

Examples of specific siloxanes (1) which are operative herein are hexamethyldisiloxane, hexabutyldisiloxane, dimethylsiloxane, phenylmethylsiloxane, ethylmethylsiloxane, vinylmethylsiloxane, divinyltetramethyldisiloxane, diphenyltetramethyldisiloxane, allylmethylsiloxane, and co-polymers of any of the above.

For the purpose of this invention the viscosity of the siloxane is not critical. However, it is preferable that they be low viscosity materials since handling is thereby facilitated.

The solvents which are employed to make the organogels of this invention include aromatic hydrocarbons, aliphatic hydrocarbons, chlorinated aliphatic and chlorinated aromatic hydrocarbons, ketones, ethers, and tertiary amines. In addition the solvents may be low viscosity siloxanes such as hexamethyldisiloxane or co-polymeric dimethyl-trimethylsiloxanes.

Organic solvents can be used for reacting the siloxanes with the organogel (2). However, the siloxane may serve both as the solvent in the organogel and as the reactant (1). Thus the preparation of the compounds of this invention may involve adding the siloxane directly to a hydrogel having the composition of compound (2). In this case the siloxane will replace the water from the hydrogel forming an organogel and at the same time will react with the silica and any $R'SiO_{1.5}$ in the organogel to form the compounds of this invention.

The temperature of the reaction is not critical and may range from say $30^\circ C.$ to the reflux temperature of the solvent or above. After reaction is complete the solvent and any excess organosilicon compound (1) are removed by evaporation or other suitable means to give the finely divided organosilicon powders of this invention.

At least a trace of either a chlorosilane or HCl or other strong acids such as H_2SO_4 or benzene sulphonic acid is present as a catalyst for the reaction. The use of a catalyst ensures that the reaction proceeds at a satisfactory rate even at room temperature.

It is believed that the reaction of the siloxane with the organogel (2) involves the formation of $\equiv SiY$ compounds *in situ*. Y is an acid anion such as Cl , $-HSO_4$, depending upon the acid catalyst used. These may either react directly with the hydroxyls on the organogel (2) in accordance with the equation $\equiv SiOH + YSiR_n \rightarrow \equiv SiOSiR_n + HY$, or they may first hydrolyse to silanols which in turn condense with the hydroxyls on organogel (2) in accordance with the equation $\equiv SiOH + HOSiR_n \rightarrow \equiv SiOSiR_n + H_2O$. The organosilyl groups of compounds (1) are chemically bonded to the silicon atoms of compound (2) by $SiOSi$ linkages.

783,868

3

The products of this invention produce a reinforcing action when incorporated in siloxane elastomers to such an extent that the elastomers have efficiencies of upwards of 150.

The efficiency of the elastomer is a product of the tensile strength in lbs./sq. in. times the percentage elongation at break, divided by 1000. This reinforcing action is not obtained with untreated xerogels nor with xerogels which have been treated with siloxanes such as hexamethyldisiloxane or dimethylsiloxane. Furthermore, the reinforcing action obtained by the products of this invention is superior to that of xerogels, fume silicas and silica xerogels which have been treated with chlorosilanes, silazanes or other reactive silanes.

The hydrophobic powders of this invention are useful for thermal insulation. They are superior therefor to other silicas due to the lack of water absorption which gives an increase in insulating value. In addition they may be employed as flattening agents in paints and as cosmetic bases.

The following examples illustrate the invention. In the examples, the methyl radical is often represented as "Me":—

EXAMPLE 1.

500 ml. of a silica hydrogel having a density of 0.107 gram of SiO_2 per ml. was broken into lumps of about 3 to 5 ml. in volume. A mixture of 1000 ml. of hexamethyldisiloxane, 250 ml. of ethanol and 75 ml. of concentrated hydrochloric acid was then added to the hydrogel. The mixture was allowed to stand for 4 hours during which time 240 ml. of an aqueous phase separated from the gel and was removed. After 24 hours, 50 ml. more of an aqueous phase separated. 100 ml. more of ethanol was then added and after 3 days 567 ml. more of an aqueous phase was removed. This aqueous phase was composed of alcohol and water which had been displaced from the hydrogel by hexamethyldisiloxane. The liquid was then decanted from the resulting organogel and the latter was dried by distillation and finally heated at 110°C . The resulting product was a soft, white powder having a bulk density of 0.12 g. per cc. and was composed of SiO_2 units having trimethylsilyl groups attached thereto.

30 parts by weight of this powder was milled with 100 parts by weight of a benzene-soluble non-flowing dimethylpolysiloxane and 3 parts by weight of tertiary butyl perbenzoate. The mixture was then heated in a mould for 15 minutes at 150°C . whereupon the resulting elastomer had a durometer reading of 32, a tensile strength of 893 lbs./sq. in. and a percentage elongation at break of 760.

EXAMPLE 2.

100 ml. of an acid silica hydrogel having a density of 0.106 g. of SiO_2 per ml. and 200 ml. of hexamethyldisiloxane were mixed in a mech-

anical mixer. After 10 days' standing at room temperature an aqueous phase had separated and was discarded. The resulting organogel was then heated to remove the excess siloxane and finally dried at 110°C . The resulting product was a dry powder having a bulk density of 0.11 g. per cc. and was composed of SiO_2 units and trimethylsilyl units linked through oxygen atoms. This material was suitable as a filler in organosiloxane elastomers.

EXAMPLE 3.

600 ml. of a silica hydrogel having a density of 0.8 gram of SiO_2 per cc. was mixed with 350 ml. of isopropyl alcohol and 250 ml. of 38 per cent hydrochloric acid and thereafter stirred for 1 hour. 1000 ml. of octamethylcyclotetrasiloxane was then added. An aqueous phase separated from the gel in 15 minutes and after 1 hour it was removed. The resulting organogel was stirred for an additional 25 minutes whereupon more water was removed. The resulting organogel was filtered from the excess siloxane and then evaporated to dryness on a steam bath and finally heated for 70 hours at 125°C . There was obtained a powder having a bulk density of 0.09 g. per cc. which was composed of SiO_2 and Me_3Si units linked to oxygen atoms. This material was suitable for use as a filler in organosiloxane rubber.

EXAMPLE 4.

600 ml. of a co-hydrogel having a density of 0.07 g. per cc. and composed of 80 mol per cent of SiO_2 and 20 mol per cent of $\text{MeSiO}_{1/2}$, was stirred for 1 hour with 350 ml. of isopropyl alcohol and 250 ml. of 38 per cent hydrochloric acid. 100 ml. of Me_3SiO

$\left[\begin{array}{c} \text{Me}_3 \\ | \\ \text{SiO} \end{array} \right]_n \text{SiMe}_3$ was then added and stirring was continued for 2 hours. The aqueous layer was then drawn off and the excess siloxane removed by distillation on a steam bath at reduced pressure. The resulting material was finally heated for 16 hours at $145\text{--}150^\circ \text{C}$. whereupon a powder having a bulk density of 0.072 gram per cc. was obtained. This powder was composed of co-polymerised SiO_2 , $\text{MeSiO}_{1/2}$, Me_3SiO and $\text{Me}_3\text{SiO}_{1/2}$ units. It is suitable for a filler in organosiloxane rubbers.

EXAMPLE 5.

660 ml. of a co-hydrogel composed of 3 mol per cent of $\text{MeSiO}_{1/2}$ and 97 mol per cent of SiO_2 and having a density of 0.078 gram of SiO_2 plus $\text{MeSiO}_{1/2}$ per ml. was mixed with 350 ml. of isopropyl alcohol and 250 ml. of 38 per cent hydrochloric acid. The mixture was stirred for $1\frac{1}{2}$ hours and then 800 ml. of hexamethyldisiloxane was added, and the mixture was again stirred for $1\frac{1}{2}$ hours. The aqueous layer which had separated from the gel was then removed and the organogel was filtered free from excess hexamethyldisiloxane

and heated for 40 hours at 110° C. The resulting material was a powder having a bulk density of 0.067 gram per cc. and was composed of copolymerised SiO_2 , $\text{MeSiO}_{1/2}$, and $\text{Me}_2\text{SiO}_{1/2}$ units. This material is suitable as a filler for organosiloxane rubber.

EXAMPLE 6.

Equivalent results were obtained when monopropylsiloxane was substituted for the monomethylsiloxane in the process of Example 5.

EXAMPLE 7.

Equivalent results were obtained when divinyltetramethyldisiloxane was substituted for the hexamethyldisiloxane in the process of Example 5.

EXAMPLE 8.

Equivalent results were obtained when monovinylsiloxane was substituted for the monomethylsiloxane in the process of Example 5.

Our Specification 28388/55 (Serial No. 783,867) of even date herewith claims a finely divided solid organosilicon compound having a bulk density of less than 0.3 g. per cc. which is a co-polymer compound of (A) from 1 to 50 mol % of $\text{RSiO}_{1/2}$ units in which R is an aliphatic hydrocarbon radical containing less than 5 carbon atoms, (B) from 4 to 30 mol % of $\text{Me}_n\text{SiO}_{1/2}$ in which n is 2 or 3 and Me

is a methyl radical and (C) from 46 to 95 mol % of SiO_2 units.

What we claim is:—

1. A process for preparing a hydrophobic organosilicon powder which comprises adding (1) an organosiloxane of the general formula

$\text{R}_n\text{SiO}_{1/2}$, in which each R is an aliphatic hydro-

carbon radical containing less than 5 carbon atoms or a phenyl radical, there being not more than one phenyl radical attached to each silicon atom and n has a value from 2 to 3 inclusive, to (2) an organogel in which at least 50 mol per cent of the polymer units are SiO_2 units, any remaining units being of the general formula $\text{R}'\text{SiO}_{1/2}$ in which R' is an aliphatic hydrocarbon radical containing less than 5 carbon atoms, said organogel (2) having a density of from 0.02 to 0.35 g. of total SiO_2 and $\text{R}'\text{SiO}_{1/2}$ per cc., and said organosiloxane (1) being present in such an amount that there is at least 0.04 organosilyl units of compound (1) per polymer unit of compound (2), in the presence of a strong acid catalyst, and thereafter removing the volatile materials from the reaction product formed during the reaction whereby a dry powdery material having a bulk density of less than 0.3 g. per cc. is obtained.

2. A process as claimed in Claim 1 wherein the organosiloxane (1) is hexamethyldisiloxane.

3. A process as claimed in Claim 1 or 2 wherein the organogel is formed *in situ* from a hydrogel during the process.

4. A process for preparing a hydrophobic organosilicon powder substantially as described with reference to any one of the examples.

ELKINGTON & FIFE,
Consulting Chemists and
Chartered Patent Agents,
Bank Chambers, 329, High Holborn,
London, W.C.1,
Agents for the Applicants.